

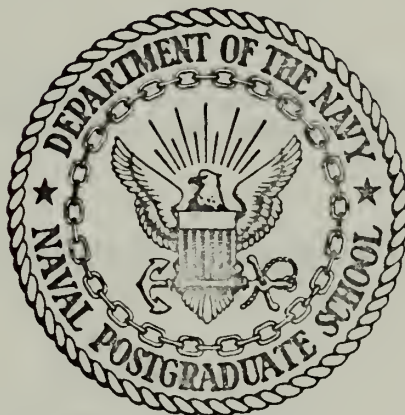
COLLISIONAL DE-EXCITATION RATES FOR THE
FIRST NEGATIVE AND SECOND POSITIVE
SYSTEMS OF NITROGEN BY WATER VAPOR

Lynn Jerome Kimball



NAVAL POSTGRADUATE SCHOOL

Monterey, California



THESIS

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NEGATIVE AND SECOND POSITIVE SYSTEMS OF
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by

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Collisional De-excitation Rates for the First Negative
and Second Positive Systems of Nitrogen by Water Vapor

by

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ABSTRACT

Nitrogen-water vapor mixtures were excited by 1.5 MeV protons from a Van De Graaff generator. Intensity versus pressure data were recorded and plotted for the first negative ($B^2\Sigma_u^+ \rightarrow X^2\Sigma_g^+$) transition ($\lambda = 3914.4\text{\AA}$), and second positive ($C^3\Pi_u \rightarrow B^3\Pi_g$) transition ($\lambda = 3371.3\text{\AA}$) in nitrogen. Theoretical equations were derived for the relative intensity as a function of pressure. Using these equations in conjunction with experimental data, the following reaction rates, k , given in units of $\text{cm}^3\text{-sec}^{-1}$, and collisional de-excitation cross sections, σ , given in units of cm^2 , were calculated: $k = 8.82 \pm 3.6 \times 10^{-10} \text{ cm}^3/\text{sec}$, $\sigma = 9.83 \pm 4.0 \times 10^{-15} \text{ cm}^2$ for the de-excitation of the $B^2\Sigma_u^+$ state of N_2^+ by H_2O ; $k = 2.02 \pm .72 \times 10^{-10} \text{ cm}^3/\text{sec}$, $\sigma = 2.26 \pm .81 \times 10^{-15} \text{ cm}^2$ for the de-excitation of the $C^3\Pi_u$ state of N_2 by H_2O .

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I. INTRODUCTION

Previous studies [1,2,3] have investigated the bombardment of molecular nitrogen alone and molecular nitrogen in conjunction with other gases by 1.0 to 2.0 MeV protons to determine the reaction rate coefficients and the de-excitation cross sections for the $(N_2)^*$ and $(N_2^+)^*$ bands. In this study, one in the series described above, an altered experimental procedure was used to investigate the quenching effects of water vapor (H_2O) on the nitrogen gas system. A stabilized water vapor pressure was maintained in the target chamber and research grade N_2 gas was added incrementally. An attached water vapor source containing singly distilled water and evacuated to a vapor pressure consistent with the ambient temperature provided the water vapor whose pressure was stabilized by allowing it to remain in the target chamber a fixed period of time before data were taken. The experiment was repeated with different amounts of water vapor pressure in the target chamber. The water vapor pressure remained constant for each experiment while the balance of the pressure was provided by N_2 gas up to a total pressure of approximately 400 torr. The target chamber was bombarded with 1.5 MeV protons and measurements were taken for each experiment. A plot of relative intensity versus pressure then provided the information required to determine the reaction rate coefficient and the de-excitation cross section for the nitrogen first negative ($B^2\Sigma_u^+ \rightarrow X^2\Sigma_g^+$) transition and the second positive ($C^3\Pi_u \rightarrow B^3\Pi_g$) transition. The de-excitation reactions are, respectively, $(N_2^+)^* + H_2O \rightarrow N_2 + H_2O + \text{energy}$ and $(N_2)^* + H_2O \rightarrow N_2 + H_2O + \text{energy}$.

II. EXPERIMENTAL PROCEDURE

A 2.0 MeV Van De Graaff electrostatic generator was used to accelerate protons into a target chamber where the gas pressure could be varied from a minimum value of about 2×10^{-6} torr to 800 torr. A block diagram of the experimental apparatus and associated electronic circuits is shown in Figure 1. The target chamber, a pyrex glass tee, was separated from the drift tube environment by a one-half mill aluminum foil window which reduced the proton beam energy to 1.25 MeV [2]. The aluminum window permitted the target gas pressure to be varied independently of the vacuum in the Van De Graaff drift tube. Attached to the target chamber was an aluminum manifold system through which the target gases were admitted. The pressure in the chamber was measured by two Wallace and Tiernan gauges, one with a 0-50 torr scale with an error of $\pm .02$ torr and the other with a 0-800 torr scale with an error of ± 5 torr.

The target chamber's vacuum system consisted of an oil diffusion pump and an independent fore pump which was also connected to the water vapor source. The water vapor source. The water vapor source was a closed pyrex glass container of approximately 1 l volume which opened to the manifold system, fore pump, and inlet funnel thru nylon stopcocks. The air in this container could be evacuated and a maximum vapor pressure of approximately 24 torr could usually be obtained.

The target gas was excited and ionized by a proton beam of about 1 microamp and energy of about 1.5 MeV. The beam terminated

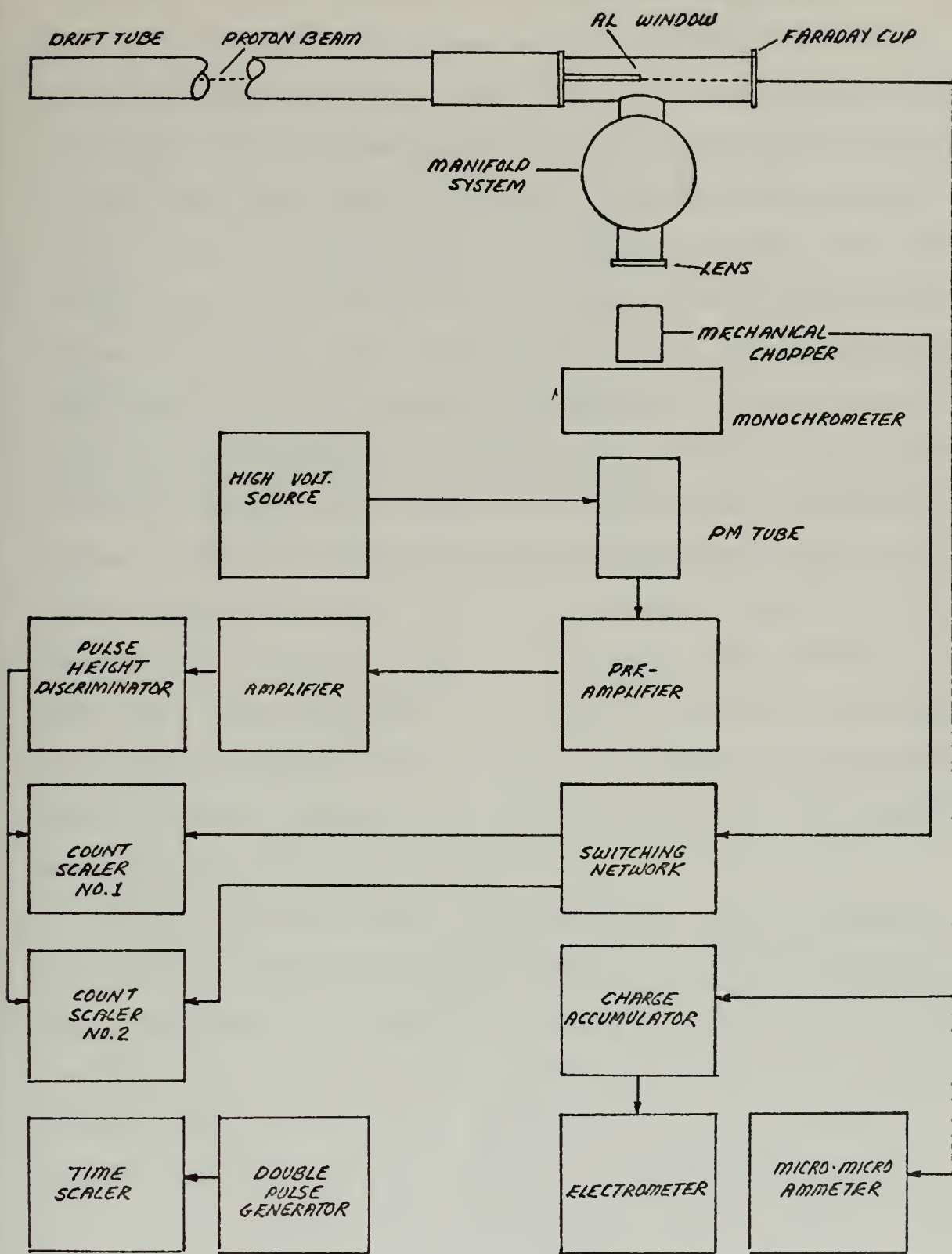
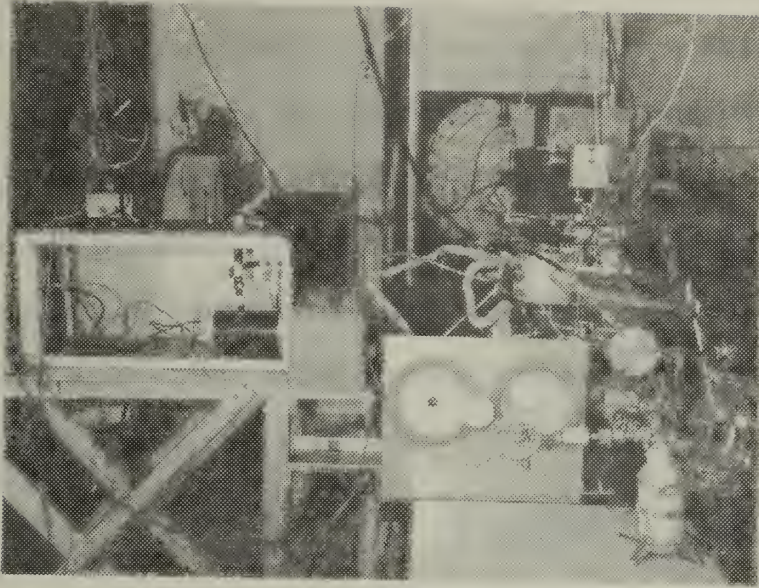


FIGURE 1. Experimental Apparatus and Associated Electronics

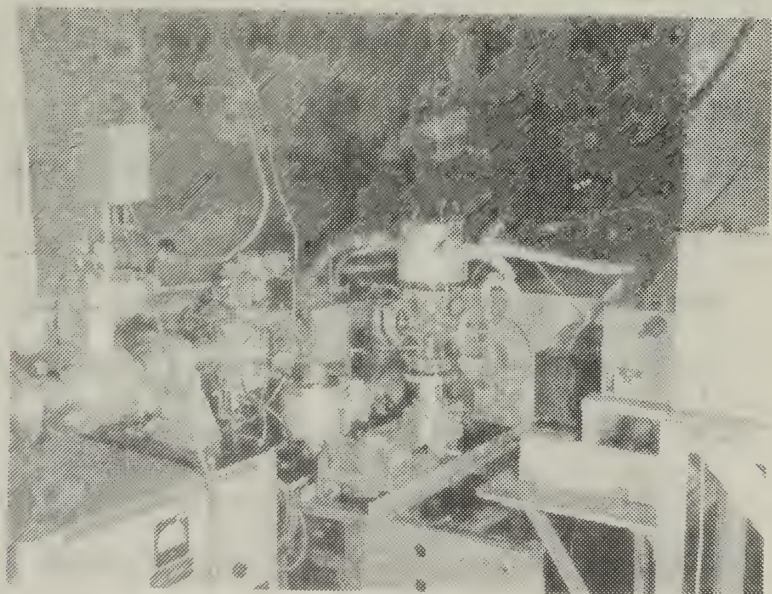
in a faraday cup and the total beam charge was accumulated in two 1 mf capacitors. The voltage was then measured by a Kiethley Instrument 150B electrometer. The intensity of the radiation from the excited target gas was measured at 90° from the proton beam by a 15 cm focal length quartz lens which focused the light through a Princeton Applied Research Model 125, mechanical chopper into the entrance slits of a Jerral Ash monochrometer which was set at the desired wavelengths. The resolving power of the monochrometer was 10\AA about the central wavelength being measured. The light then passed into an Electro Optics Associates type PM-101 cooled photomultiplier assembly with a Dumont 6467 pm tube which counted the photons. From the pm tube the electrical pulses were sent to an Ortec preamplifier, model 101; then to a Canberra amplifier, model 810; and from there to a Canberra pulse height discriminator, model 830. The monochrometer was aligned to the desired wavelength by sending the output of the pm tube to a Princeton Applied Research lock-in amplifier, model H-8, so the spectral line signal could be peaked prior to the experimental run.

Leaving the discriminator, the pulses went into two Canberra scalers which were controlled by a transistorized switching network. The scalers were gated such that one scaler counted during the period of time that the pm tube was receiving light from the target chamber, and the other scaler counted during the dark periods when the pm tube was shielded by the mechanical chopper. Thus one scaler counted photons, background and dark current pulses while the other scaler counted only dark current and background pulses. Concurrently, another Canberra scaler served as a clock by counting time pulses. All three scalers were also manually



*FIGURE 2. Target Chamber and Target Area Instrumentation
Front View*

*FIGURE 3. Target Chamber and Target Area Instrumentation
Rear View*



gated such that when a specific charge was recorded on the KI 150B electrometer, the counting and timing scalers were stopped and the proton beam was interrupted by a solenoid. The overall system dead time was calculated to be approximately 1.75×10^{-6} sec.

Using the apparatus described above, relative intensity (I) versus pressure (P) data was recorded and plotted. Intensity was determined in part by counting the individual photons given off by the reacting gases. From the corrected photon count (TC), the relative intensity (I) was determined to be

$$I = \frac{TC}{Q} \quad (1)$$

where (Q) represents the specific charge indicated by the KI 150B when the scalers were stopped. The corrected photon count was determined to be

$$TC = \frac{c}{1 - \frac{c}{t} \tau} - DC \quad (2)$$

where (c) represents the scaler count of photons, background and dark current, and (DC) represents the scaler count of only background and dark current. The count (c) was in turn corrected for dead time by the expressions in the denominator. Here (t) represents the counting period in seconds and (τ) the system dead time. To reduce the dark current resulting from thermionic emissions the pm assembly was cooled by a liquid nitrogen cooling system.

Since the counting rate could be varied by changing the beam current, the proton beam was maximized on the KI 410 micro-microammeter using the focus adjust at the beginning of each experiment. A maximized signal and an appropriate pulse height discriminator setting then assured a suitable signal to noise ratio. The proton energy was maintained at an energy of approximately 1.5 MeV during

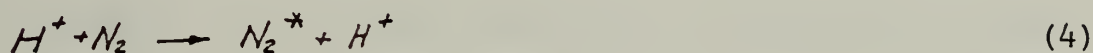
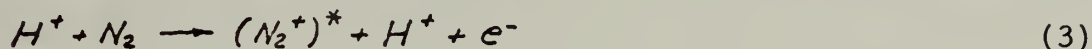
each experiment and for any one counting period the pressure remained constant. The temperature of the target gases likewise remained constant during each counting period. The accumulated proton charge varied somewhat with each counting period because of the manual gating which likewise varied the counting times. With the aid of a Hewlett Packard 9100A calculator and 9125A calculator plotter, relative intensity versus pressure curves were plotted for the various experimental data and are found in Figures 4 through 11. Both the molecular nitrogen first negative and second positive band systems were used. The slits on the monochromator through which the light passed were perpendicular to the beam path and so situated in conjunction with the quartz lens that only the reaction spectrum within 1 to 2 mm of the aluminum window was passed into the monochromator. In this region, the energy loss of the beam was negligible.

The target gas was nitrogen and water vapor mixed together at predetermined pressures. The standard experimental procedure was to admit water vapor into the reaction chamber and permit the vapor pressure to stabilize over a period of about one hour. This delay was necessitated by the absorption of the water vapor into the aluminum and glass components of the target chamber. With the water pressure stabilized, research grade nitrogen was added to the target chamber in increments up to a maximum of approximately 400 torr. Before each incremental increase in pressure, pressure and intensity data were recorded. The Hewlett Packard 9100A calculator was also used for data reduction and theoretical calculations.

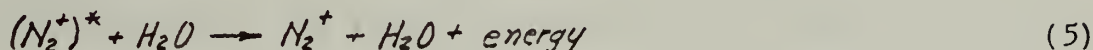
III. THEORY

A. BACKGROUND

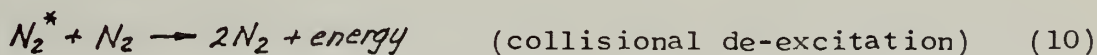
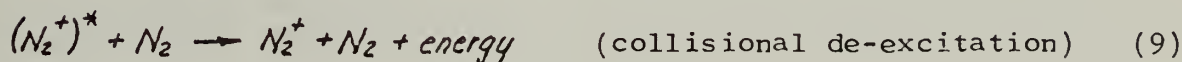
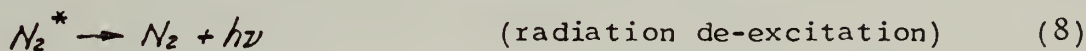
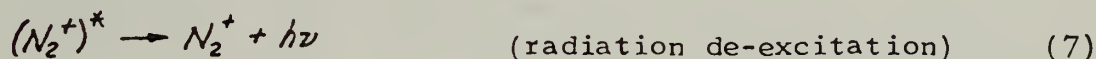
Since a nitrogen gas-water vapor mixture was used as the target gas, the following excitation reactions could occur upon proton (H^+) impact



The primary de-excitation reactions of the nitrogen first negative and second positive systems are as follows:



The above represent those reactions specifically resulting from the presence of water vapor. In addition, the following reactions occur independently. The reactions are accompanied by the primary causation mechanism [4]:



The general rate equation given below with appropriate assumptions was used to develop a set of theoretical equations from which the collisional de-excitation rate and the reaction cross section could be computed. It represents the rate of transition to and from a specific state.

$$\frac{dN_k^*}{dt} = \rho v N \sigma_k + \sum_{l>k} \lambda_{lk} N_l^* - \sum_{k>i} \lambda_{ki} N_k^* - \sum_j N_k^* k_j n_j + \sum_m \sum_n N_n k_{mn} n_m^* \quad (11)$$

where

1. $\rho v N \sigma_k$ direct excitation to state k by protons (H^+) where σ_k is the excitation cross section, ρ is the proton beam density, N is the target density and v the proton velocity.
2. $\sum_{l>k} \lambda_{lk} N_l^*$ transitions from higher state l into state k where λ_{lk} is the transition probability of decay from state l into state k and N_l^* , is the number density of excited particles in state l.
3. $\sum_{k>i} \lambda_{ki} N_k^*$ radiative loss by transitions from state k to lower state; where λ_{ki} is the transition probability of decay from state k into state l and N_k^* is the number density of excited particles in state k.
4. $\sum_j N_k^* k_j n_j$ collisional de-excitation of state k with particles n_j where k_j is the collisional de-excitation rate and n_j is the number density of particles of type j.
5. $\sum_m \sum_n N_n k_{mn} n_m^*$ collisional excitation to state k by collisions with m type particles in excited states n_m^* where n_m^* is the number density of particles in the excited state, k_{mn} is the collisional excitation rate, and N_n is the density of target particles.

In order to get the general rate equation into a usable form, the following assumptions were made.

1. $\rho v N \sigma_k = R_k$ proportional to pressure (p) in target chamber.
2. N^* proportional to intensity (I).
3. n_j proportional to partial pressure (p_j).
4. $\sum_k \lambda_{ki} = \lambda$ constant for spectral line under study.
5. $\sum_j k_j = k$ constant for spectral line under study.
6. Ideal gas law valid in the pressure ranges used. It is generally held that the ideal gas law holds out to several atmospheres of pressure for most atmosphere gases; thus, the assumption that the ideal gas law is the equation of state is valid to a high degree [5]. It can also be shown then that since $p_j = n_j kT$, the number density of particles of type j (n_j) is indeed proportional to the partial pressure of gas j (p_j).

The first term was assumed to be a function only of the target gas pressure in the target chamber. This necessitated holding the incident proton beam energy constant during each experiment in order that the excitation cross sections which are energy dependent be considered constant for a given transition.

Transitions to states above k as reflected in the second term could result from direct interaction with the incident proton beam. This process was assumed to be proportional to the target gas pressure and hence was considered additive to the first term to simplify the rate equation.

In the third and fourth terms, it was assumed that the transition probabilities were constant for the spectral line under study and that the number density of target gas particles N_k^* was proportional to the intensity (I).

The fifth term applies to collisional excitation and is eliminated from the rate equation because the excitation energy of the water molecules is insufficient to excite the nitrogen molecules. The latter assumption is also validated by the marked reduction in intensity when water vapor is mixed with nitrogen gas in increasing amounts. If the water vapor at reaction chamber temperatures transferred any energy to nitrogen an enhancement of the nitrogen spectrum would have been observed.

Under conditions of equilibrium where excitation to state k is equal to de-excitation from state k and the above assumptions are applied, the general rate equation reduces to the form

$$\frac{dN_k^*}{dt} = 0 = R_k - \lambda N_k^* - k_j n_j N_k^* \quad (12)$$

or

$$aP = \lambda bI + k_j \frac{b}{kT} P I \quad (13)$$

where $R_k = aP$, $N_k = bI$ and $n_j = \frac{P_j}{kT}$
from the ideal gas law at constant volume.

B. NITROGEN WITH WATER VAPOR PRESENT

Research grade nitrogen was incrementally added to water vapor from singly distilled water and the resulting bombardment by protons created excited states in N_2 gas, equations (3) and (4). The initial experimental results indicated that the presence of water vapor acted to quench the $(N_2)^*$ and $(N_2^+)^*$ states by a much larger collisional de-excitation rate than that obtained with nitrogen alone [3].

Using the general rate equation with the assumptions listed in the previous section:

$$R_K = \lambda N_K^* + N_K^* (K_{N_2} n_{N_2} + K_{H_2O} n_{H_2O}) \quad (14)$$

or

$$a P_{N_2} = \lambda b I + b I \left(\frac{K_{N_2} P_{N_2}}{KT} + \frac{K_{H_2O} P_{H_2O}}{KT} \right) \quad (15)$$

and thus

$$P_{N_2} = \frac{\lambda b}{a} I + \frac{b}{a} \frac{I}{KT} (K_{N_2} P_{N_2} + K_{H_2O} P_{H_2O}) \quad (16)$$

This equation attempts to explain the behavior of the de-excitation of $(N_2)^*$ and $(N_2^+)^*$ in view of equations (12) and (13), and can be further reduced to:

$$P_{N_2} = A' I + (B P_{N_2} + C P_{H_2O}) I \quad (17)$$

where in light of previous assumptions,

$$A' = \frac{\lambda b}{a} \quad B = \frac{b}{a} \frac{K_{N_2}}{KT}$$

and

$$C = \frac{b}{a} \frac{K_{H_2O}}{KT}$$

Equation (17) can be modified to provide an experimental means by which the unknown constants can be determined. First, a preliminary rearrangement yields

$$\frac{P_{N_2}}{I} = (A' + C P_{H_2O}) + B P_{N_2} \quad (18)$$

or

$$\frac{P_{N_2}}{I} = A + B P_{N_2} \quad (19)$$

with p_{N_2} (p_{N_2} found from $p_{N_2} = p - p_{H_2O}$) and I known, plotting $p_{N_2/I}$ versus p_{N_2} for each incremental point resulted in a straight line over the pressures used. The constant A is found as the intercept of the plot with the $p_{N_2/I}$ axis and B is found as its slope. (A Hewlett Packard 9100A calculator was used in the above calculations.)

In addition, it is known that the ratio B/A' remains invariant within experimental error from experiment to experiment [2] so the value of A can be determined by

$$A' = B \left(\frac{A'}{B} \right) \quad (20)$$

and thus the value of C can be found

$$C = \frac{A - A'}{p_{H_2O}} \quad (21)$$

The only variables which now remain are intensity and total pressure. An equation which expresses their relation can be written

$$I = \frac{p_{N_2}}{(A' + Bp_{N_2}) + Cp_{H_2O}} \quad (22)$$

Using this equation and the values of the constants obtained as above, intensities at various pressures were calculated and a theory curve was superimposed on the experimental points resulting from equation (1). A comparison of the predicted intensities shows excellent graphical correlation between experiment and theory.

The collisional de-excitation reaction rate for water vapor (K_{H_2O}) can be calculated as follows:

$$C = \frac{b}{a} \frac{K_{H_2O}}{KT} \quad (23)$$

$$K_{H_2O} = C \frac{KT}{A'\gamma} \quad (23)$$

where the radiative lifetime, τ , is the reciprocal of the decay probability λ . Since there is one equation with two unknowns, K_{H_2O} and τ , to determine K required first establishing values of τ .

Bennett and Dalby experimentally found the value of τ for the first negative (3914.4Å) and the second position (3371.3Å) band systems.

These values are, respectively, $\tau = 6.58 \times 10^{-8}$ sec's and $\tau = 4.45 \times 10^{-8}$ sec's [6]. A dimensional analysis of equation (19) yields the units of A' to be (sec-cm⁻³) and B and C to be (sec-erg⁻¹) which is in agreement with equation (24).

The collisional de-excitation cross section (σ_d) can be calculated from $N^* k_j n_j = N^* \sigma_d \phi_j$ where ϕ_j is the flux of particles of type j and σ_d represents the probability that a de-excitation collision will occur. But $\phi_j = \bar{v}_r n_j$ where \bar{v}_r is the mean relative velocity between particles. Thus

$$N^* k_j n_j = N^* \sigma_d \bar{v}_r n_j \quad (25)$$

or

$$\sigma_{H_2O} = \frac{K_{H_2O}}{\bar{v}_r} \quad (26)$$

where

$$\bar{v}_r = \left[\frac{8KT(m_1+m_2)}{\pi m_1 m_2} \right]^{1/2} \quad (27)$$

for the nitrogen gas water vapor mixture. Masses m_1 and m_2 are the masses of nitrogen and water vapor, respectively [7].

IV. RESULTS

A. GENERAL

Below is a summary of the results obtained in this research for the collisional de-excitation reaction rates and the respective cross sections. A search through the current literature revealed no data concerning the nitrogen water vapor collisional de-excitation reactions to include as comparisons.

Transition	3914 $\overset{\circ}{\text{A}}$	3371 $\overset{\circ}{\text{A}}$
$K_{\text{H}_2\text{O}}(\text{cm}^3\text{-sec}^{-1})$	$8.82 \pm 3.6 \times 10^{-10}$	$2.02 \pm .72 \times 10^{-10}$
$\sigma_{\text{H}_2\text{O}}(\text{cm}^2)$	$9.83 \pm 4.0 \times 10^{-15}$	$2.26 \pm .81 \times 10^{-15}$

TABLE I. Reaction Rates (K) and De-excitation Cross Sections (σ)

The experimental relationship of the intensity versus pressure is shown by Figures 4 through 11 for the first negative ($\lambda = 3914.4\overset{\circ}{\text{A}}$) and the second positive ($\lambda = 3371.3\overset{\circ}{\text{A}}$) transitions. Pressure/Intensity versus pressure plots are shown in Figures 12 and 13. The values of the de-excitation reaction rates and cross sections were found using equations (24) and (26). These values were verified by a comparison of the theoretical computation using equation (22) with the experimental results found in Figures 4 through 13 for the various target gas pressures.

B. DISCUSSION

The assumptions made in arriving at equation (18) seem to be valid in light of the close correlation between the experimental

results and the theoretical equations. Secondary excitation effects, such as excitation by high energy electrons and soft x-rays were neglected in arriving at equation (18). It was assumed that the only excitation processes were direct, and that this was proportional to the pressure of the target gas.

It was found that the second positive band system responded exactly in the same manner to proton bombardment as the first negative system. The relative intensity of the two lines increased at a decreasing rate with increasing N_2 gas pressure up until a total target gas pressure of approximately 100 torr after which the intensity increased slightly at a constant rate. The lines of the second positive transition however were observed to increase in intensity at a lesser rate than the first negative.

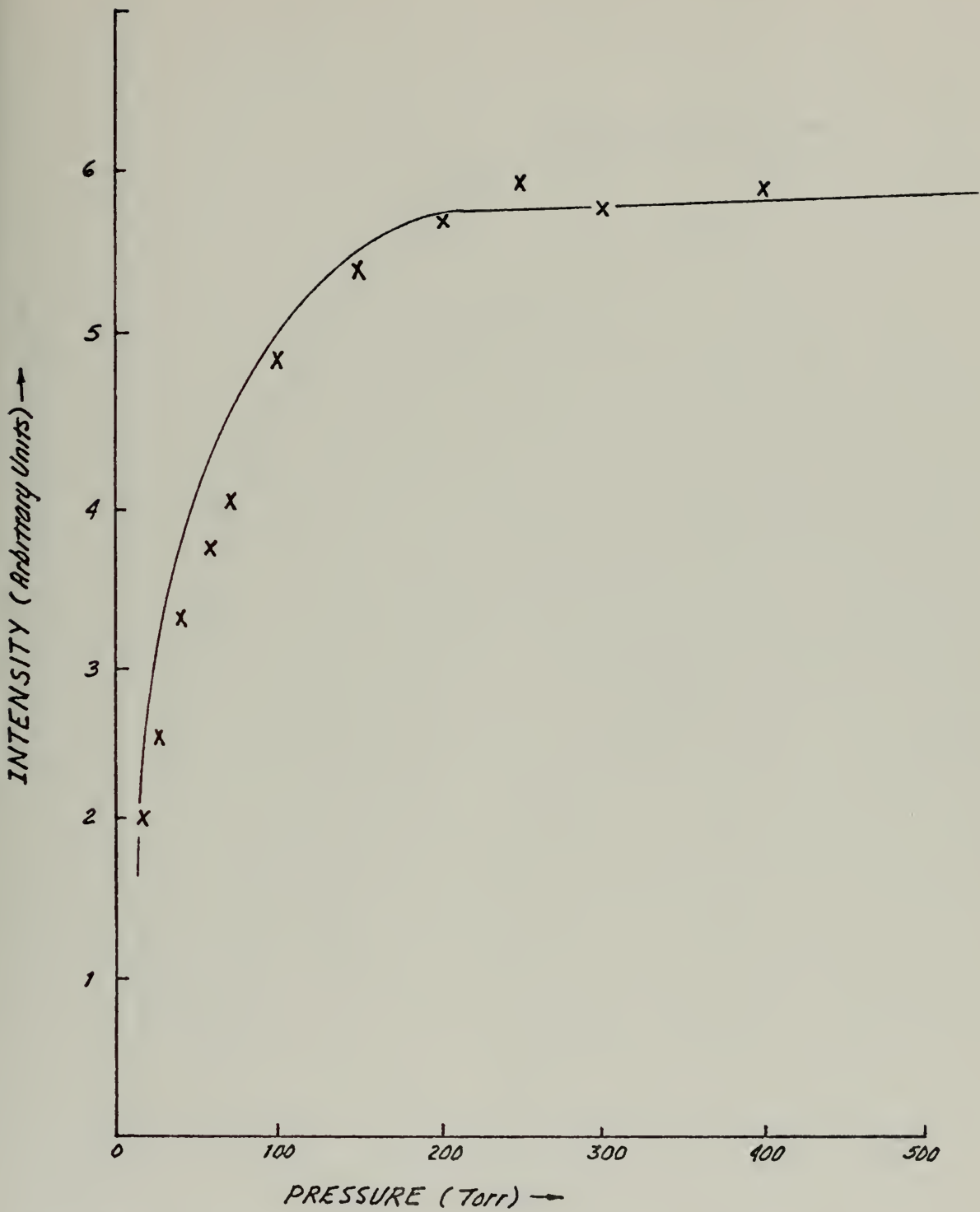


FIGURE 4. Intensity versus Pressure (3914\AA). H^+ on 4.2 Torr H_2O , Balance N_2 . Experimental Data (x), Theory Comparison.

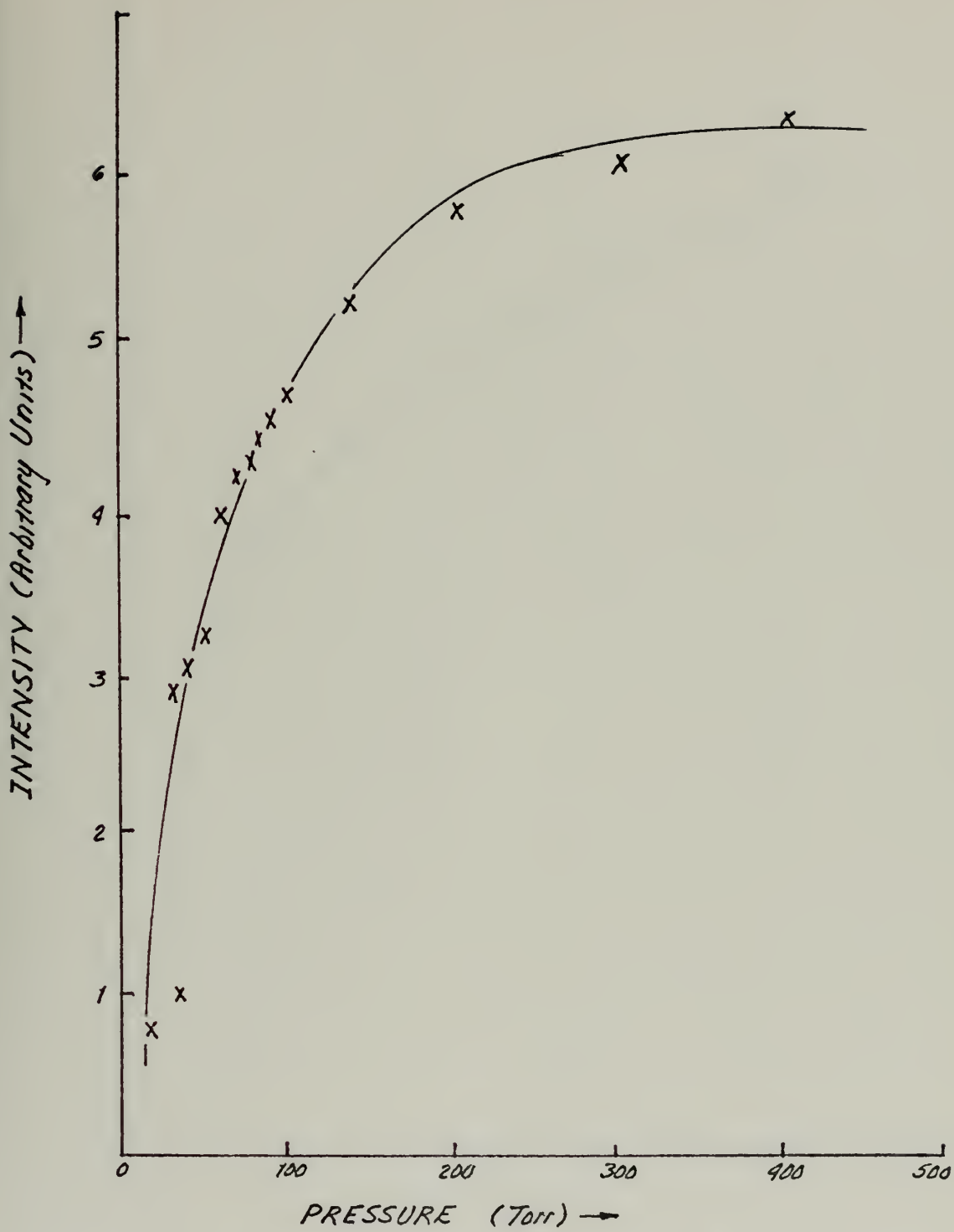


FIGURE 5. Intensity versus Pressure (3914\AA). H^+ on 11.2 Torr H_2O , Balance N_2 . Experimental Data (X), Theory Comparison.

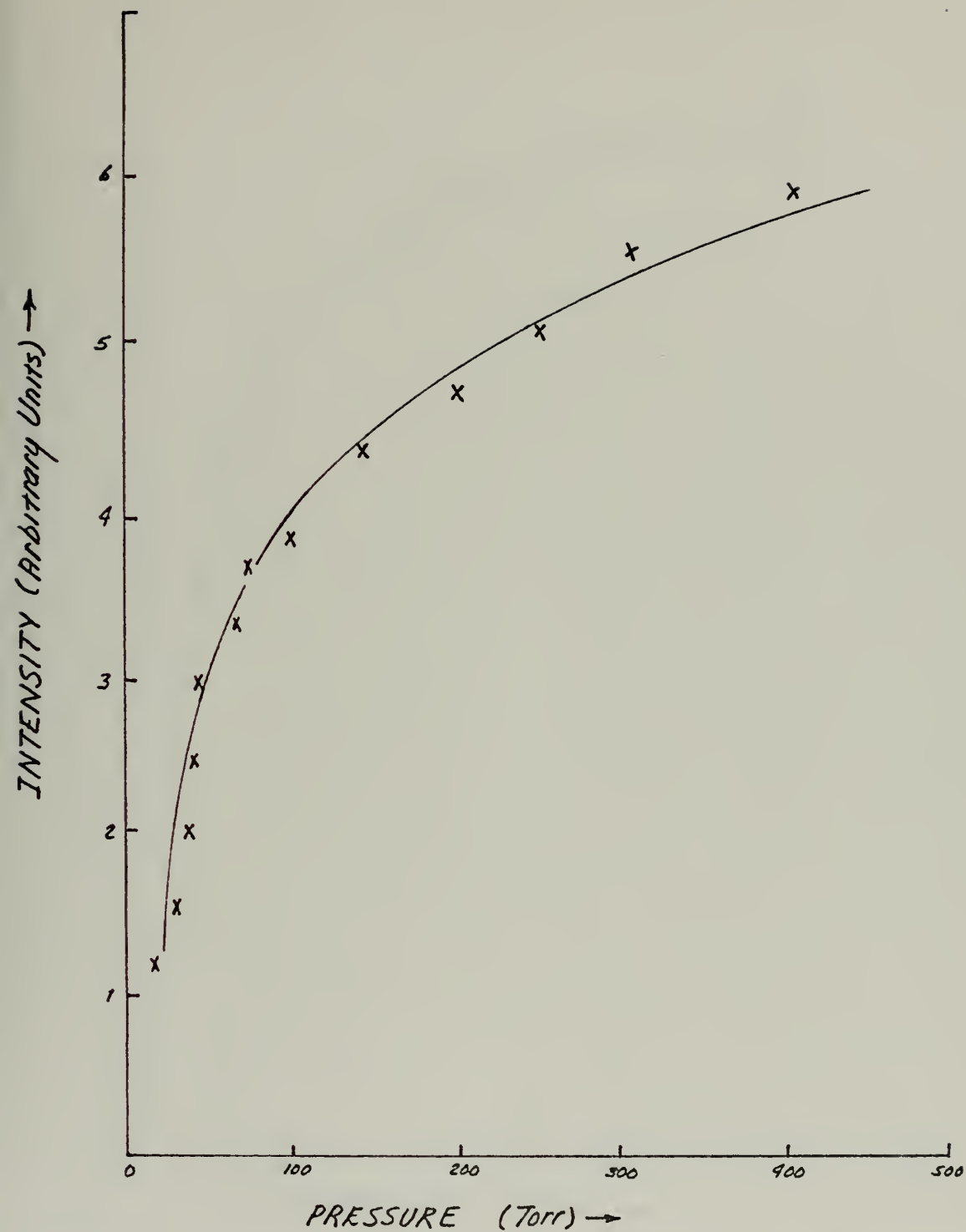


FIGURE 6. Intensity versus Pressure (3914 \AA). H^+ on 15.8 Torr H_2O , Balance N_2 . Experimental Data (x), Theory Comparison.

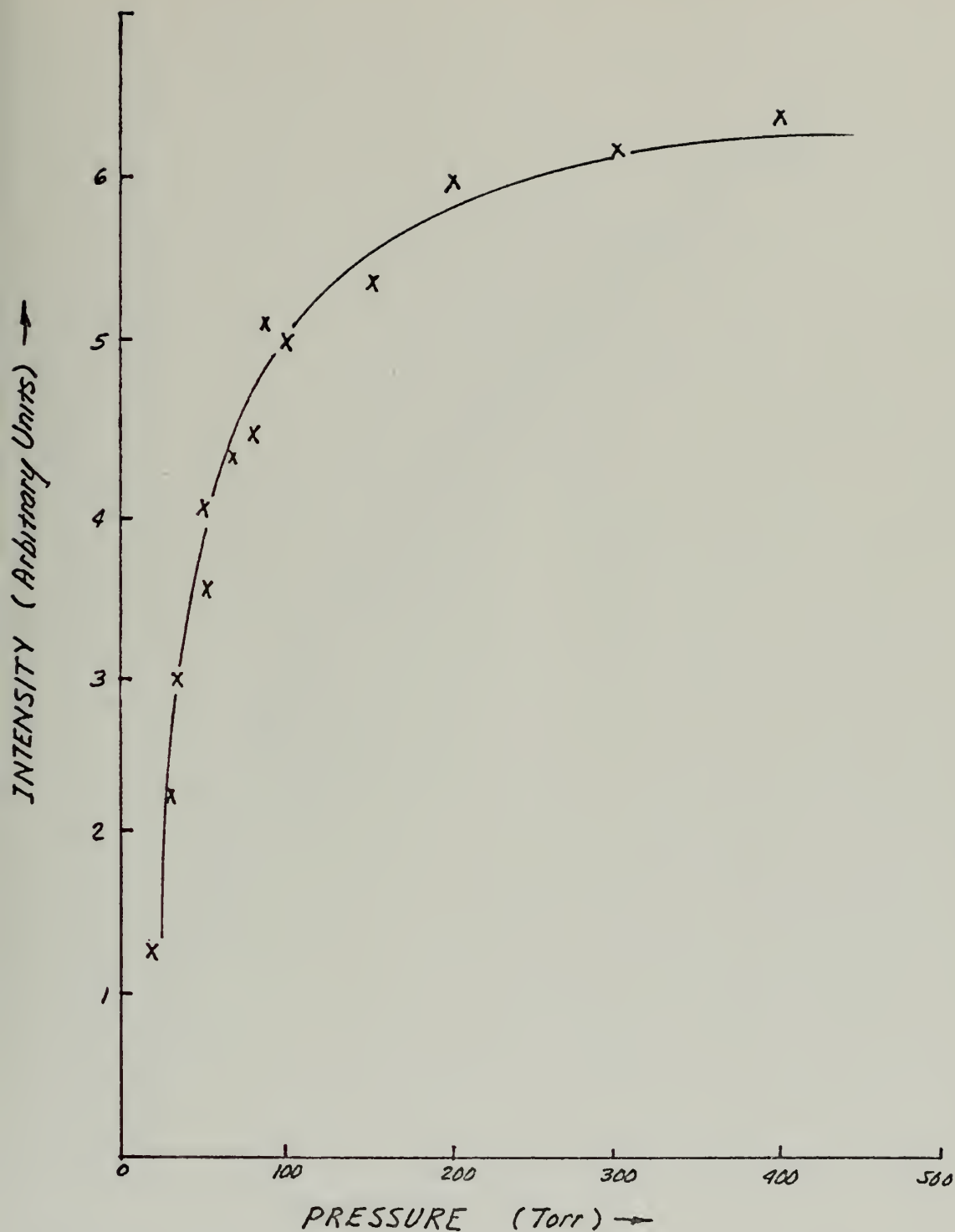


FIGURE 7. Intensity versus Pressure (3914\AA). H^+ on 22.0 Torr H_2O , Balance N_2 . Experimental Data (x), Theory Comparison.

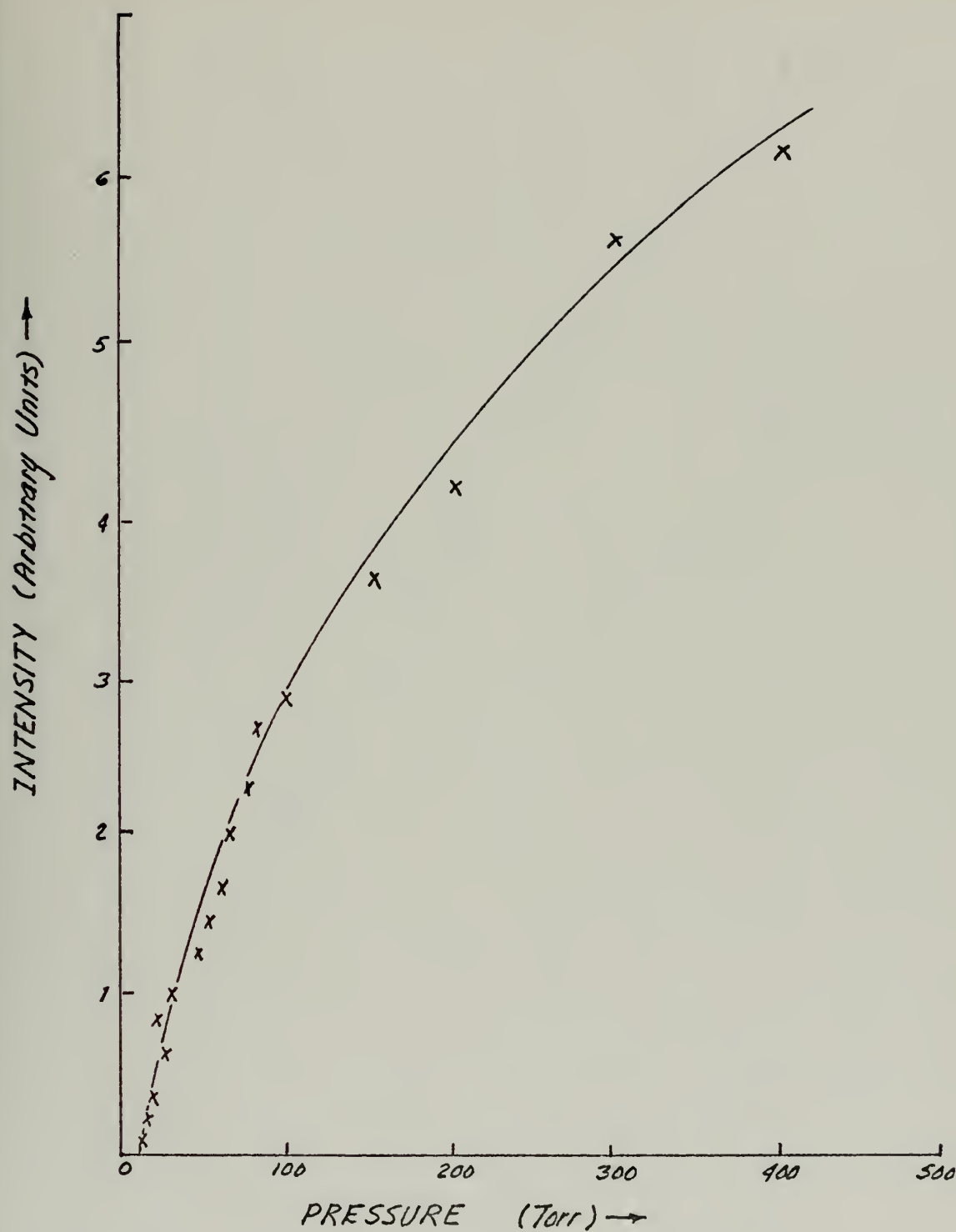


FIGURE 8. Intensity versus Pressure (3371 \AA). H^+ on 4.3 Torr H_2O , Balance N_2 . Experimental Data (x), Theory Comparison.

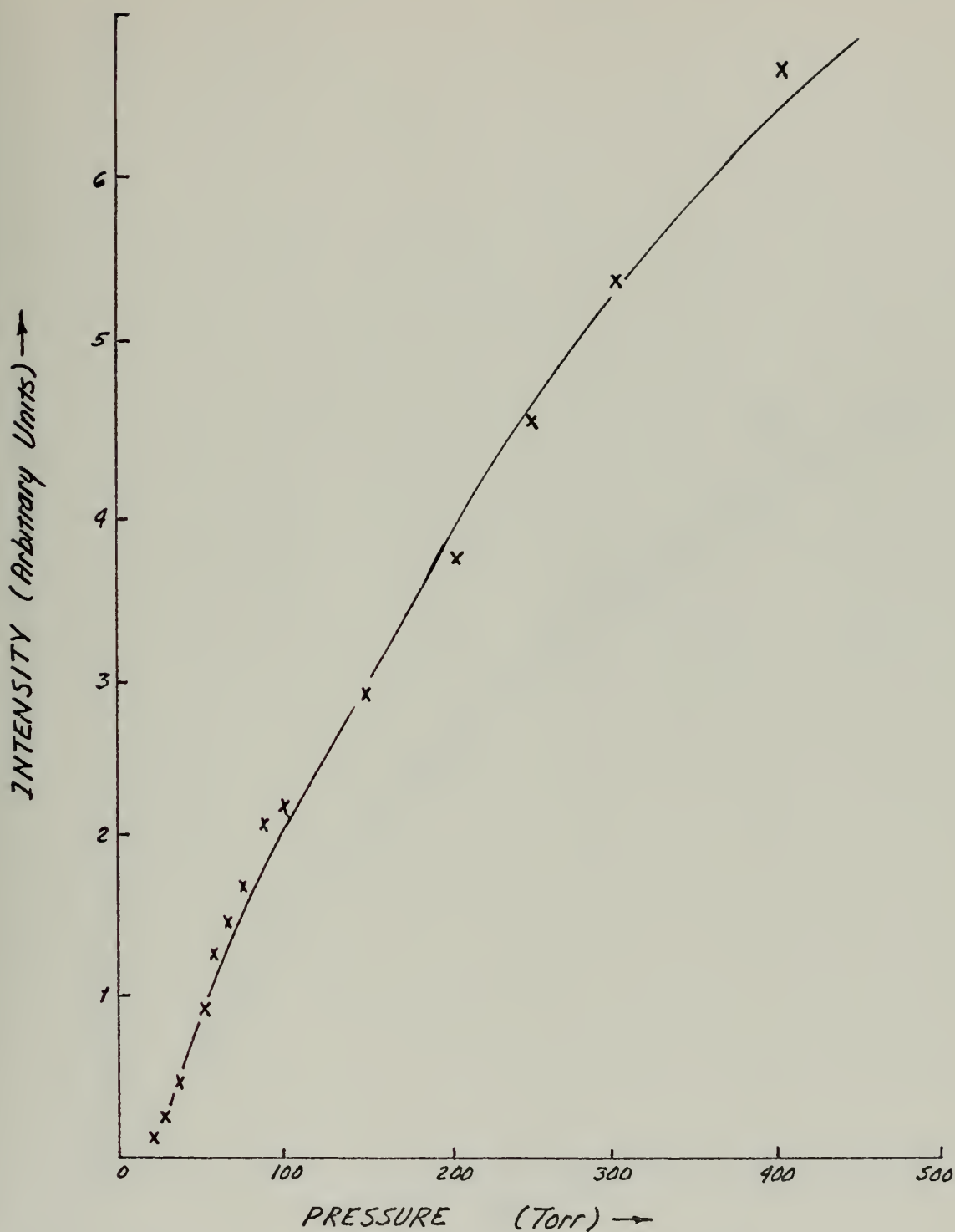


FIGURE 9. Intensity versus Pressure (3371 Å). H^+ on 77.0 Torr H_2O , Balance N_2 . Experimental Data (x), Theory Comparison.

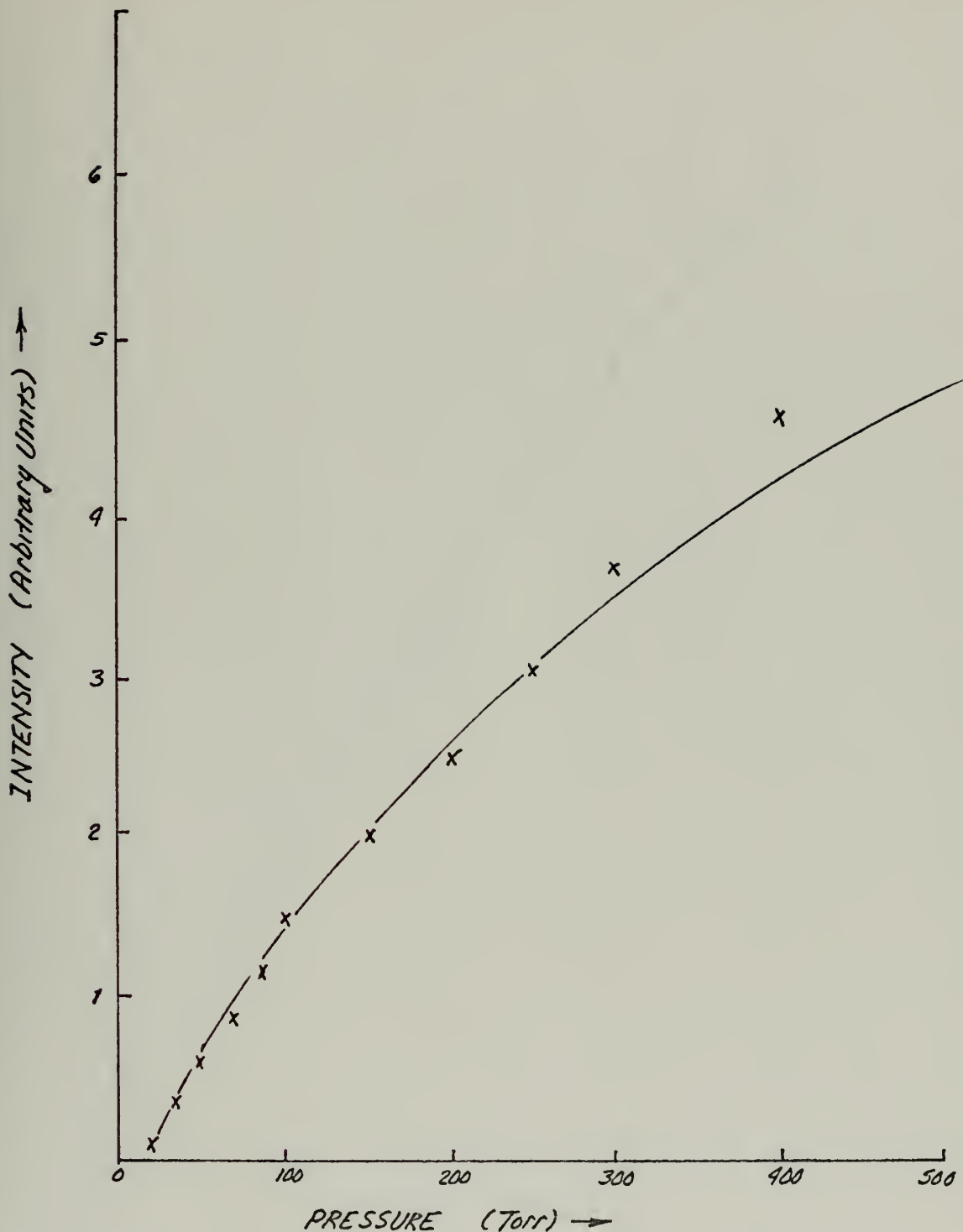


FIGURE 10. Intensity versus Pressure (3371 Å). H⁺ on 15.8 Torr H₂O, Balance N₂. Experimental Data (x), Theory Comparison.

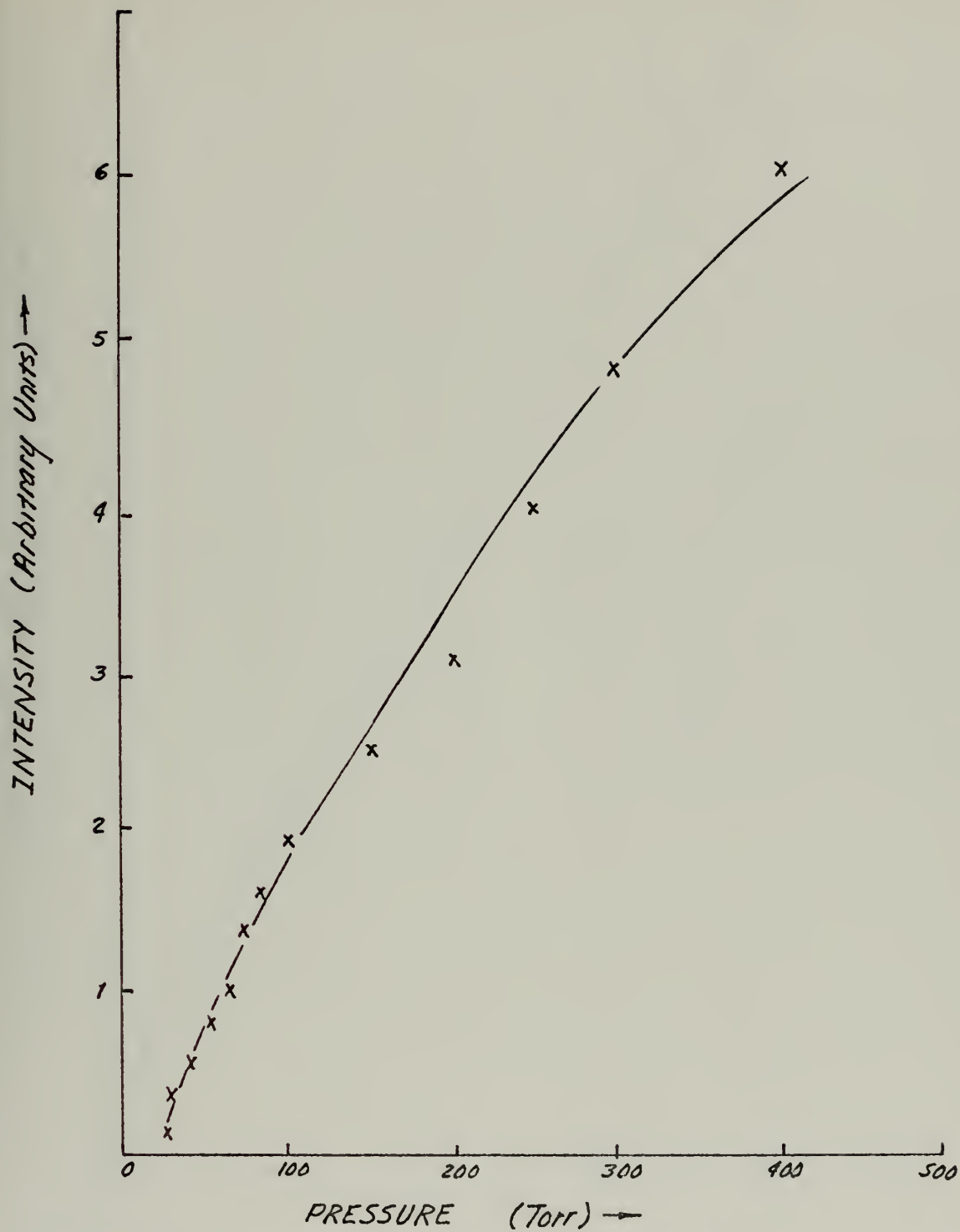


FIGURE 11. Intensity versus Pressure (3371 \AA). H^+ on 22.0 Torr H_2O , Balance N_2 . Experimental Data (x), Theory Comparison.

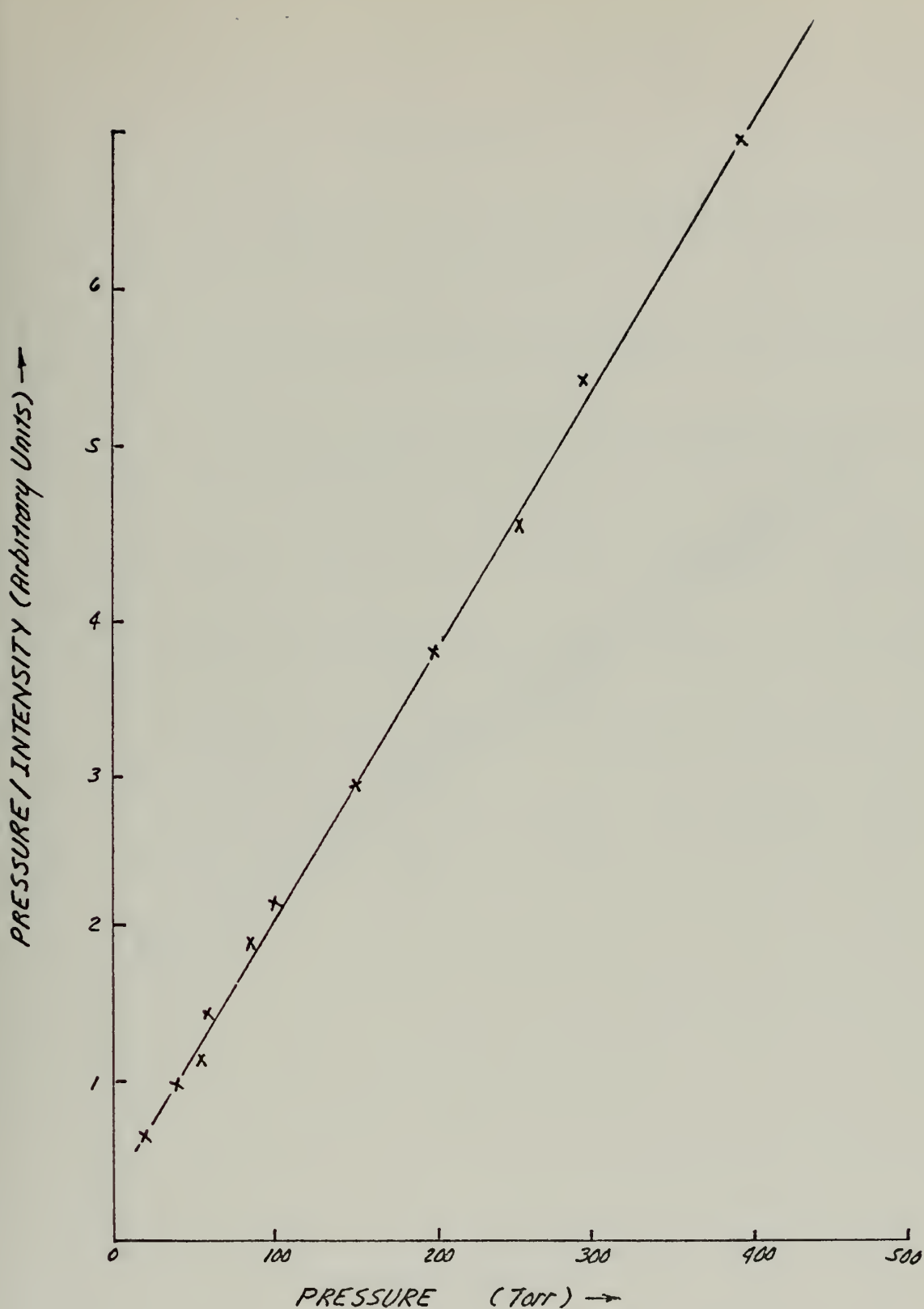


FIGURE 12. Pressure / Intensity versus Pressure (3914 \AA). H^+ on 4.2 Torr H_2O , Balance N_2 . Experimental Data (x), Theory Comparison.

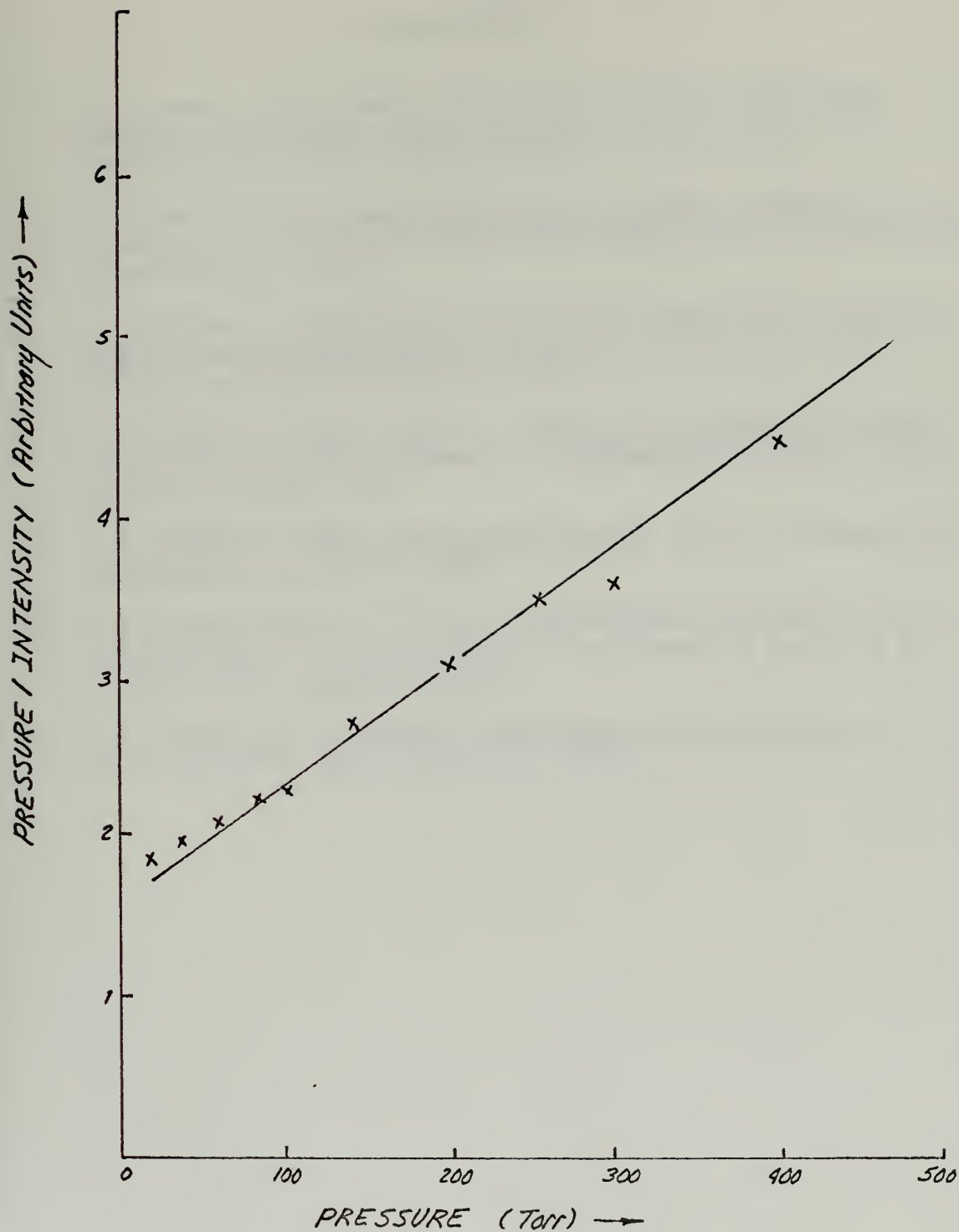


FIGURE 13. Pressure/Intensity versus Pressure (3371 Å). H⁺ on 4.3 Torr H₂O, Balance N₂. Experimental data (x), Theory Comparison.

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13. ABSTRACT
Nitrogen-water vapor mixtures were excited by 1.5 MeV protons from a Van De Graaff generator. Intensity versus pressure data were recorded and plotted for the first negative ($B^2\Sigma_u^+ \rightarrow X^2\Sigma_g^+$) transition ($\lambda = 3914.4\text{\AA}$), and second positive ($C^3\Pi_u \rightarrow B^3\Pi_g$) transition ($\lambda = 3371.3\text{\AA}$) in nitrogen. Theoretical equations were derived for the relative intensity as a function of pressure. Using these equations in conjunction with experimental data, the following reaction rates, k , given in units of $\text{cm}^3\text{-sec}^{-1}$, and collisional de-excitation cross sections, σ , given in units of cm^2 , were calculated: $k = 8.82 \pm 3.6 \times 10^{-10} \text{ cm}^3/\text{sec}$, $\sigma = 9.83 \pm 4.0 \times 10^{-15} \text{ cm}^2$ for the de-excitation of the $B^2\Sigma_u^+$ state of N_2^+ by H_2O ; $k = 2.02 \pm .72 \times 10^{-10} \text{ cm}^3/\text{sec}$, $\sigma = 2.26 \pm .81 \times 10^{-15} \text{ cm}^2$ for the de-excitation of the $C^3\Pi_u$ state of N_2 by H_2O .

KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
Nitrogen						
Nitrogen-Water Vapor						
Collisional de-excitation						
Cross-sections						
Reaction rate						

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